Long Range Binding in Alkali-Helium Pairs

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Variational calculations are performed to search for bound rovibrational states of diatomic molecules formed from alkali atoms and helium in the very shallow $^2\Sigma$ electronic ground state. Examination of a recent set of potential surfaces and several older potentials indicates that all pairs possess a single very diffuse bound state with $J = 0$. Such marginally bound states will have profound effects on low energy collisions between alkali atoms and helium atoms. The sensitivity of these states with respect to retardation effects has been studied. The variational calculations employ a basis set of generalized Laguerre functions and new analytical expressions for kinetic energy matrix elements.

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Molecular species with a marginally bound quantum mechanical ground state are of special interest because they exhibit unusual scattering properties and are candidates for the formation of three body systems which might show the Efimov effect [1–3]. The long range of the wave function associated with such a state implies distant correlations which are relevant for the formation of Bose condensates [4]. The existence of marginally bound states in alkali-helium pairs might be an important factor for sympathetic cooling [5,6].

Alkali metals have been known for a long time to have very weak interactions with helium with typical well depths of 0.5–1.5 cm^{-1} at pair separations of 6–8 Å [7]. Mainly the repulsive branches of these potentials have been characterized with experimental methods while the low collision energies needed to gain information on the well region are not easily accessible [7,8]. The shallowness of the wells has led to the widespread belief that they do not support bound states. This reasoning may be partly due to the fact that the much deeper He-He well ($D_e = 7.6\ \mathrm{cm}^{-1}$) was predicted to support only a single bound state around $10^{-3}\ \mathrm{cm}^{-1}$ [9] for ^{4}He pairs while ^{3}He-^{4}He does not possess a bound state. The existence of the ^{4}He dimer was confirmed only recently in experiments with extremely cold jet expansions [10,11]. The predicted expectation value for the He-He distance of about 50 Å for the best pair potentials [9] is in fair agreement with an experimental value obtained from a measurement of the transmission of a helium beam through a nanostructure grid [12]. The diffuseness of the wave function makes it sensitive to relativistic effects like retardation which modify the long range part of the interaction and thereby affect the binding energy [9,13–15]. The mixed trimer ^{3}He^{4}He$_2$ is known to be bound [3,16], and even though it is a very delocalized system its binding energy is already about $10^{-2}\ \mathrm{cm}^{-1}$.

In a recent diffusion Monte Carlo (DMC) study of alkali atoms attached to large ^{4}He$_n$ clusters [16] we investigated the critical helium cluster size n where binding of a sodium atom occurs. To our surprise a bound state with binding energies between 0.01 and 0.02 cm^{-1} depending on the potential model already appeared at $n = 1$, the ^{4}He-^{23}Na dimer. This observation of a bound state for ^{4}He-Na and ^{4}He-Li was confirmed in a recent calculation by Yuan and Lin [17]. However, no systematic search for bound states of alkali-helium pairs on the available potential surfaces [7,18–21] has been undertaken before. Initial simple basis set expansion and grid calculations failed to confirm the DMC result. The challenges involved in the accurate calculation of such diffuse wave functions have motivated the search for novel approaches like mapped Fourier methods [22]. This Letter reports accurate variational results for all alkali metal and helium combinations which were obtained after careful choice of a proper basis set with correct asymptotic properties.

The bulk of the present calculations were carried out with the recently published series of alkali atom-helium interaction potentials [18] which were determined with the surface integral method by Kleinekathöfer, Tang, Toennies, and Yiu (KTTY potential). This method has proven to be accurate for other long range potentials like He$_2$, Ne$_2$, and Ar$_2$ [23]. The mathematically complicated original form of the heteronuclear potentials does not lend itself to easy and efficient implementation. We used a least squares fit to potential values computed with the original form to recast it into a simpler modified Tang-Toennies form,

$$V(r) = A \exp(-b_1 r - b_2 r^2) - \sum_{n=3}^{8} f_{2n}(b'(r), r)\, \frac{C_{2n}}{r^{2n}}\,, \tag{1}$$

where f_{2n} is a Tang-Toennies damping function and $b'(r) = b_1 + 2b_2 r$ [24]. Optimal values for A, b_1, and b_2 were determined by fitting to the original potential in the region between 10 and 20 bohr, including the most important region for bound state calculations, with fixed dispersion coefficients to ensure proper asymptotic properties. Values for C_6–C_{10} were taken from Ref. [18]

except for He-Li, for which probably more accurate coefficients from [25] were used. The higher coefficients are defined through the conventional recursion relation $C_{2n+2} = (C_{2n}/C_{2n-2})^3 C_{2n-4}$. The parameters $A, b_1, b_2, C_6, C_8, C_{10}$ for the representation of the potentials from Ref. [18] are collected in Table I. This parametrization deviates from the original by at most 0.6% in the value of the well depth. This is well below the uncertainty margin of the potential itself which can be estimated by comparison with other potential models due to Patil [19] and Cvetko *et al.* [20]. In order to check the sensitivity of the results with respect to the potential model, variational calculations were done for all of these potentials and for a Lennard-Jones model, which was used in the study of interactions of alkali atoms with liquid helium [26].

The huge range of the wave function expected for the alkali-helium dimers requires a careful choice of basis functions. Since much of the wave function is in the nonclassical region it is desirable to employ basis functions which have the correct asymptotic behavior. In the case of the weakly bound HeHF complex convergence problems have been noticed with asymptotically improper basis functions [27]. Based on previous algebraic studies and numerical tests [28] a basis of orthonormalized generalized Laguerre functions $\tilde{L}_n^\alpha(x)$ was chosen. This type of function,

$$\tilde{L}_n^\alpha(x) = \left\{ \frac{n!}{\Gamma(n + \alpha + 1)} \right\}^{1/2} e^{-x/2} x^{\alpha/2} L_n^\alpha(x) , \qquad (2)$$

where $L_n^\alpha(x)$ is a generalized Laguerre polynomial [29] and $\alpha > -1$, has the proper single exponential behavior at long range. The shape of this basis can be tuned through the order α and through a variable transformation which relates the dimensionless variable x to the particle distance r according to $x = k(r - r_0)$. While k affects the range of the basis, r_0 shifts its origin, such that the functions span the range $[r_0, \infty]$. Potential energy matrix elements are evaluated through high order Gauss-Laguerre quadrature. High accuracy even for basis sets of several hundred functions is achieved by starting the recurrence relation used for the computation of the normalized Laguerre polynomials $\tilde{L}_n^\alpha(x_i)$ with the square root of the Gaussian weights w_i, such that the recursion directly generates $\sqrt{w_i}\,\tilde{L}_n^\alpha(x_i)$ [28]:

$$\langle \tilde{L}_n^\alpha | V | \tilde{L}_m^\alpha \rangle \approx \sum_{i=1} \sqrt{w_i}\,\tilde{L}_n^\alpha(x_i) V(x_i) \sqrt{w_i}\,\tilde{L}_m^\alpha(x_i) . \qquad (3)$$

TABLE I. Parameters for the alkali helium KTTY potentials [Eq. (1)]. All parameters in atomic units.

Pair	A	b_1	b_2	C_6	C_8	C_{10}
He-Li	2.430 857	1.049 11	0.003 812 98	22.507	1083.2	72 602.1
He-Na	2.218 564	1.008 72	0.003 990 53	23.768	1307.6	94 563.2
He-K	1.568 281	0.869 41	0.004 662 13	34.038	2525.2	237 538
He-Rb	1.440 646	0.838 39	0.004 824 56	36.289	2979.0	300 406
He-Cs	1.440 646	0.838 39	0.004 824 56	41.417	3903.4	453 443

Repeated application of the derivative operator on the Laguerre basis leads to a formula which expresses the matrix elements of the kinetic energy operator through matrix elements of x^{-1} and x^{-2}. For these integrals new analytical formulas which allow efficient evaluation through a stable recurrence relation have been derived and implemented [28].

The variational energies were calculated through expansion into basis sets of 100–400 Laguerre functions. Extensive convergence tests were made with respect to the size of the basis and the basis parameters α, k, and r_0. The parameters were varied in the range $2 \leq \alpha \leq 10$, $0.25 \leq k \leq 2, 0.2 \leq r_0 \leq 2$. Convergence was typically achieved with 200 functions. The correctness of the results was verified by test calculations for the helium dimer, variational calculations with a modified Laguerre basis using $x = kr^2$ [see Eq. (2)], and calculations with the standard Fourier-grid Hamiltonian method [30] and an optimized Numerov-Cooley code for selected cases. The grid based methods performed well for ^{4}He-^{23}Na, but convergence could be achieved only with very large grids for the more diffuse species requiring up to 2 orders of magnitude more computer time than the Laguerre basis calculations. The variational results agree very well with our DMC results. Details of our implementation of the DMC method are given in previous publications [31]. Statistical errors were quantified by careful autocorrelation analysis. Systematic errors due to finite time steps and trial wave function bias were checked by time step variation and calculations with different trial functions.

Table II lists all systems and isotopic combinations for which a bound state was found with the presently available potentials [18–20]. Expectation values of the pair distance, of the kinetic energy, and of the ground state (Ψ_0) rotational constant B_0 computed as $\langle \Psi_0 | \hbar^2 / 2\mu r^2 | \Psi_0 \rangle$ are reported in Table III only for the present KTTY potential. A full set of properties including expectation values for the other potentials, scattering lengths, and effective ranges will be published elsewhere, together with a comprehensive discussion of the available potentials [35].

The B_0 values (cf. Table III) typically amount to 10 times the binding energy, largely ruling out bound excited rotational states. The direct search for bound $J > 0$ states was unsuccessful. As expected, the interparticle distance increases in proportion to the inverse square root of the binding energy. At the same time the kinetic energy expectation value goes down, indicating the smoother wave functions. The well depth is greatest for He-Li and decreases monotonically for the heavier alkali metals for all potential models. The increasing reduced mass partially compensates this trend and causes binding to be strongest for He-Na (KTTY) or He-Rb (Patil, Cvetko *et al.*). While the available potential models predict a bound state for almost all of the ^{4}He-alkali combinations, the existence of ^{3}He-alkali bound states is more ambiguous. None of these potential models gives a

TABLE II. Ground state energies for several recent alkali-helium pair potentials from variational calculations. Atomic masses from Ref. [32] were used. Missing entries indicate that no bound state was found. All energies in cm^{-1}.

Pair	μ/amu	KTTY	Cvetko [20]	Patil [19]	LJ [a]
^{4}He-^{6}Li	2.403 355	−0.001 053			
^{4}He-^{7}Li	2.548 623	−0.003 907		−0.000 516	
^{4}He-^{23}Na	3.409 071	−0.020 142 [b]	−0.016 074	−0.017 005	−0.010 914
^{4}He-^{39}K	3.629 734	−0.007 786 [b]	−0.021 232	−0.021 774	−0.015 290
^{4}He-^{40}K	3.638 217	−0.007 941	−0.021 522	−0.022 033	−0.015 508
^{4}He-^{41}K	3.646 303	−0.008 091	−0.021 799	−0.022 281	−0.015 718
^{4}He-^{85}Rb	3.822 421	−0.007 140	−0.036 680	−0.035 053	−0.025 763
^{4}He-^{87}Rb	3.826 379	−0.007 202	−0.036 840	−0.035 194	−0.025 885
^{4}He-^{133}Cs	3.885 584	−0.003 437	−0.026 534	−0.024 611	−0.018 119
^{3}He-^{23}Na	2.666 245	−0.000 863 [b]		−0.000 472	
^{3}He-^{39}K	2.799 343		−0.000 825	−0.002 117	−0.000 485
^{3}He-^{40}K	2.804 386		−0.000 875	−0.002 184	−0.000 517
^{3}He-^{41}K	2.809 188		−0.000 924	−0.002 250	−0.000 549
^{3}He-^{85}Rb	2.912 576		−0.005 650	−0.007 027	−0.003 224
^{3}He-^{87}Rb	2.914 874		−0.005 704	−0.007 080	−0.003 260
^{3}He-^{133}Cs	2.949 105		−0.002 746	−0.003 421	−0.001 294

[a] Lennard-Jones 6/12 potential with well depth ϵ and r_m as given in Table I of Ref. [26].
[b] The Fourier grid method gives −0.020 142 for ^{4}He-^{23}Na, −0.007 786 for ^{4}He-^{39}K, and −0.000 861 for ^{3}He-^{23}Na. DMC gives -0.0205 ± 0.0003 for ^{4}He-^{23}Na.

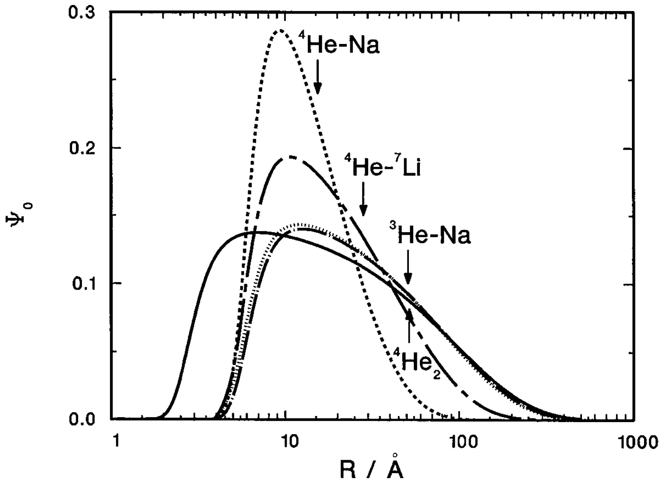

FIG. 1. Ground state wave functions for selected alkali-helium pairs from variational calculations on the KTTY potential without retardation. The ^{4}He-^{6}Li wave function almost coincides with ^{3}He-Na and is indicated by the thin dotted curve. Helium dimer (solid line) is shown for comparison. Arrows indicate $\langle r \rangle$ expectation values. Note the logarithmic distance scale.

bound state for ^{3}He-Li. Wave functions for ^{4}He-Li and He-Na isotopomers are shown in Fig. 1. Calculations for ^{4}He-^{6}Li with the older dispersion coefficients [18] gave a binding energy of only 0.000 084 cm^{-1}.

The weakness of the binding in all these systems requires careful consideration of several subtle and often neglected effects, namely, the validity of the Born-Oppenheimer approximation [36,37], spin orbit effects, and the relativistic retardation effect [13–15]. For $^4He_2$ a decrease of the binding energy by about 10% due to retardation has been predicted [9,13]. The influence of retardation is, however, expected to be generally smaller for the present systems due to their lower lying dipole excitations. In the absence of precise data for the retardation correction we adopted the model of O'Carroll and Sucher [34] to estimate the switching between the r^{-6} and r^{-7} leading dispersion interaction. This model has been previously found to perform very well also for $^4He_2$ [15]. Using available polarizabilities [38] to compute C_7 values according to Ref. [34] and the C_6 values from Table I we checked the retardation effect for ^{4}He-^{6}Li, ^{4}He-^{7}Li, ^{3}He-^{23}Na, and ^{4}He-^{23}Na. The fractional changes of the binding energies and the distance expectation values of ^{4}He-^{6}Li and ^{3}He-^{23}Na are comparable to $^4He_2$, but the bound states persist (see Table III). The effect on the other two species is smaller but noticeable.

TABLE III. Well depths V_{min}, ground state energies E_0, equilibrium distance r_{min}, and expectation values for the pair separation $\langle r \rangle$, ground state rotational constant $\langle B_0 \rangle$, and kinetic energy $\langle T \rangle$ from variational calculations with the KTTY potential. Energies and B_0 in cm^{-1}, distances in Å.

Pair	V_{min}	E_0	r_{min}	$\langle r \rangle$	$\langle B_0 \rangle$	$\langle T \rangle$
^{4}He-^{6}Li	−1.5425	−0.001 053	6.16	48.53	0.017 42	0.033 457
^{4}He-^{6}Li [a]	−1.5389	−0.000 958	6.16	50.51	0.016 77	0.031 905
^{4}He-^{7}Li	−1.5425	−0.003 907	6.16	28.15	0.027 83	0.063 601
^{4}He-^{7}Li [a]	−1.5389	−0.003 722	6.16	28.66	0.027 33	0.062 056
^{4}He-^{23}Na	−1.2974	−0.020 142	6.43	15.41	0.037 20	0.125 440
^{4}He-^{23}Na [a]	−1.2940	−0.019 703	6.43	15.50	0.036 96	0.124 048
^{3}He-^{23}Na	−1.2974	−0.000 863	6.43	50.85	0.014 37	0.027 745
^{3}He-^{23}Na [a]	−1.2940	−0.000 775	6.43	53.21	0.013 76	0.026 288
^{4}He-^{39}K	−0.8984	−0.007 786	7.30	20.95	0.022 29	0.066 310
^{4}He-^{40}K	−0.8984	−0.007 941	7.30	20.81	0.022 40	0.066 924
^{4}He-^{41}K	−0.8984	−0.008 091	7.30	20.68	0.022 49	0.067 507
^{4}He-^{85}Rb	−0.8129	−0.007 140	7.53	21.43	0.020 08	0.060 342
^{4}He-^{87}Rb	−0.8129	−0.007 202	7.53	21.37	0.020 12	0.060 588
^{4}He-^{133}Cs	−0.6916	−0.003 437	7.95	27.38	0.014 53	0.039 176
$^4He_2$ [33]	−7.635	−0.000 918	2.97	51.68	0.042 21	0.069 649

[a] Including retardation according to [34] using $C_7^{\text{HeLi}} = 56\,888$ a.u., $C_7^{\text{HeNa}} = 55\,223$ a.u.

The use of atomic masses in vibrational calculations instead of nuclear masses is often justified as providing a good correction for non Born-Oppenheimer effects [39]. Using nuclear masses instead of atomic masses caused only very minor effects on our binding energy results. This can be easily understood since a change of the masses mainly affects the very small kinetic energy expectation values (see Table III). Direct calculations of corrections beyond the Born-Oppenheimer approximation by *ab initio* methods are exceedingly difficult for such weakly bound species. Adiabatic corrections were very recently found to increase the binding energy of $^4He_2$ by about 10% [37], which would largely cancel out the retardation effect. Similar calculations for mixed alkali-helium systems would be even more challenging. Deformations of the ground electronic $^2\Sigma$ potential curves by spin-orbit interaction with the excited $^2\Sigma$ and $^2\Pi$ states correlating with the ^2P atomic states appear unlikely to be strong enough to qualitatively change our results due to the large energetic separation of about 2 eV.

Experimental verifications of the present predictions will be challenging. The diffraction technique used for the helium dimer [11] is an elegant tool for the unequivocal identification of fragile species in a molecular beam, but the jet coexpansion works only for very volatile species. A recent comparison of calculated refractive indices of sodium atomic waves with experimental observations that ^{4}He-^{23}Na might, indeed, possess a bound state [40]. The experimental observation of a zero-energy resonance has been reported recently for collisions between cesium atoms at μK temperatures [41].

While extremely long range wave functions already appear in the ground state of the present diatomics, they are expected to occur for any molecular system at energies very close to the dissociation limit. Calculations aiming at exact quantum densities of states [42] near threshold should therefore incorporate a proper description of such states which might be relevant for reaction dynamics due to their unusual scattering properties.

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